

# Continuous-Fiber, Malleable Thermoset Composites with Sub-1-Minute Dwell Times: Validation of Impact Performance and Evaluation of the Efficacy of the Compression Forming Process

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1:15:00 PM EDT  
Project ID: mat147



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# Overview

## Timeline

- Project Start: 9/2018
- Project End: 8/2020
- Percentage complete: 75%

## Budget

- Total project funding: \$ 1 M
  - DOE share: \$ 500,000
  - Contractor share: \$ 500,000
- FY 2018: \$325,000
- FY 2019: \$575,000
- FY 2020: \$100,000

## Barriers Addressed<sup>1</sup>

- Low cost, high volume manufacturing of carbon fiber composites, with cycle time < 3 minutes.
- Non-destructive evaluation of malleable thermoset composites- specifically acoustic approach to QA/QC.
- Enhancing crash energy management.

*1. 2017 U.S. DRIVE MTT Roadmap Report, sections 4 and 5*

## Partners

- Mallinda (lead): Philip Taynton
- PNNL: Michael Larche/ Leo Fifield
- SNL: Bo Song
- ORNL: Robert Norris

Any proposed future work is subject to change based on funding levels

# Relevance

IMPACT	APPROACH
Under 1-minute dwell times	Precured malleable thermoset prepregs
Non-destructive evaluation	Acoustic microscopy towards QA/QC
Crash energy management	Material development informed by split Hopkinson high speed impact testing, & automotive crash-worthiness testing

(TMAC)

## OBJECTIVES

- Develop malleable thermoset resin/fiber combinations for improved crash energy management
- Study the relationship between compression forming conditions, acoustic response, and defects & voids in the composite
- Utilize high speed split-Hopkinson impact testing to characterize candidate composite materials
- TMAC results to demonstrate feasible >20% light weighting of CEM structures vs. Al

# Approach - Resin Background

## Imine-linked malleable thermoset polymers, a.k.a. vitrimers

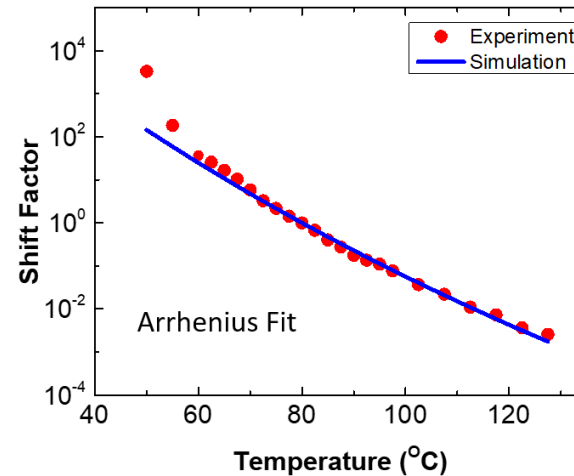
### Thermoset-level mechanical strength

38% v/v resin, CF UD 2585-12K	Mallinda Vitrimers	Hexcel Snapcure
Tensile Modulus (GPa)	119	118
Ultimate Tensile (GPa)	2.0	2.2
Flexural modulus (GPa)	124	114
Ultimate Flex (GPa)	1.3	1.5
Compression modulus (GPa)	118	123
Ultimate compression (GPa)	1.5	1.65
Ultimate shear (MPa)	78	89
Tg (DMA Loss Modulus)	130 °C	125 °C
In-mold dwell time	20 sec – 1min	10 min – 120 min

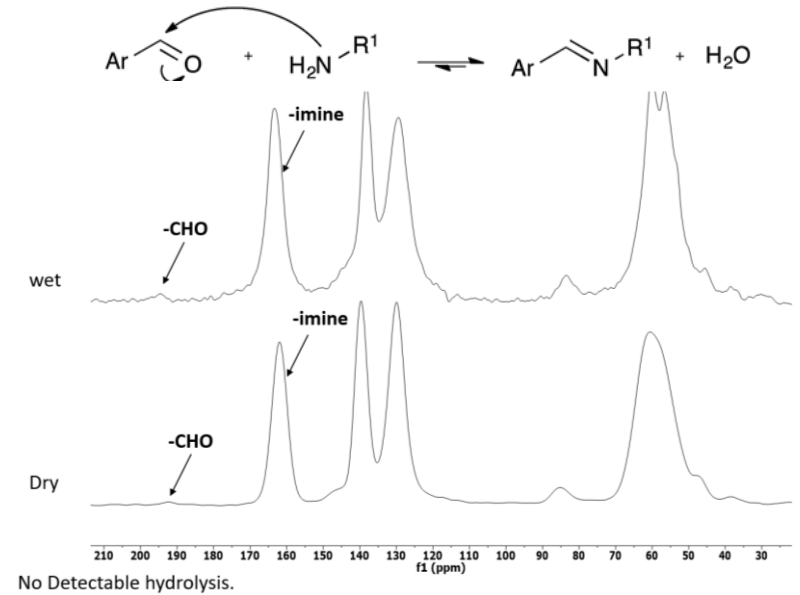
Relaxation modulus  $\tau = \frac{1}{k} \exp\left(\frac{E_a}{RT}\right)$

constants  $k$   $E_a$   $RT$  Temperature

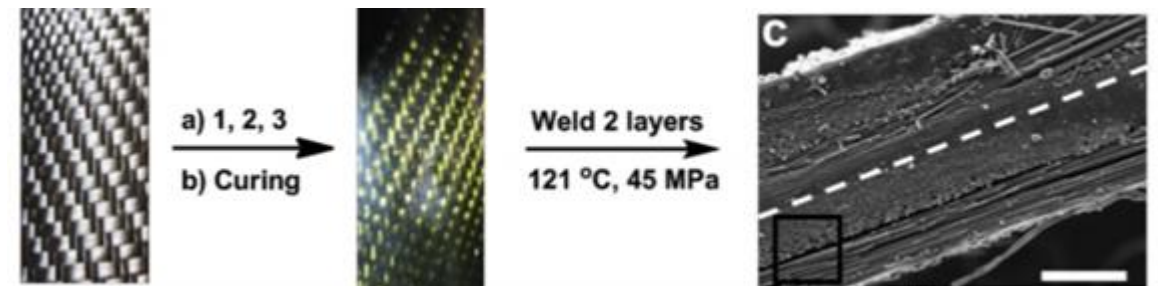
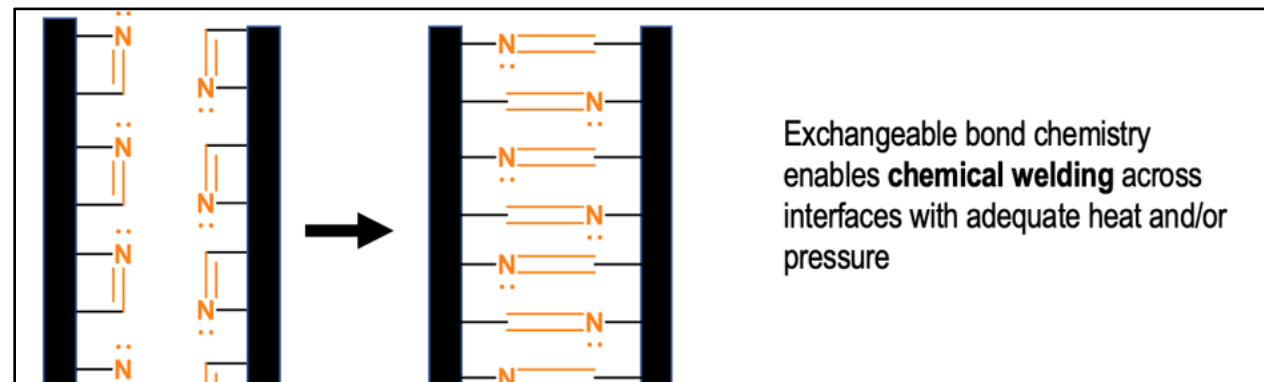
Activation energy of Bond Exchange Reaction



### Hydrolytic stability is key to practical applications



### Stress-relaxation behavior & weldability of vitrimers correlated to covalent bond exchange reaction



Adv. Mater. 2014, 26, 3938–3942.

# Approach - Resin Background

## Industrial Processing



Scale-up of vitrimer resin synthesis



Towpreg

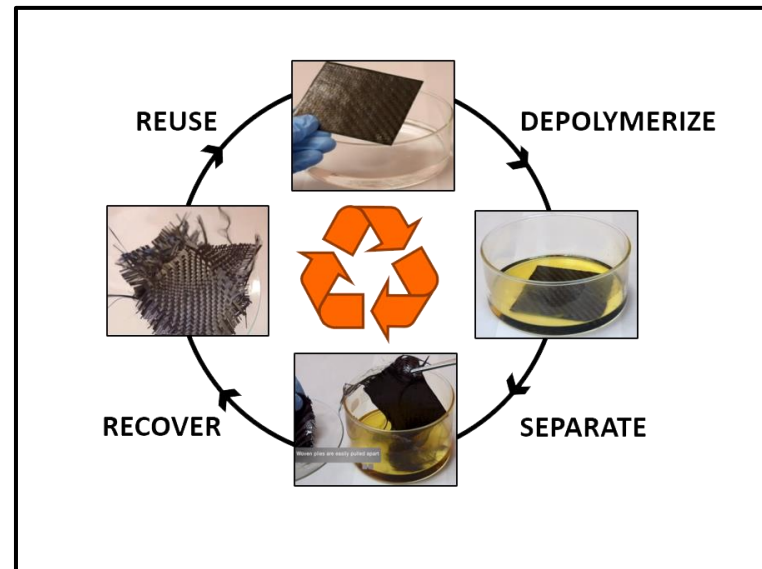
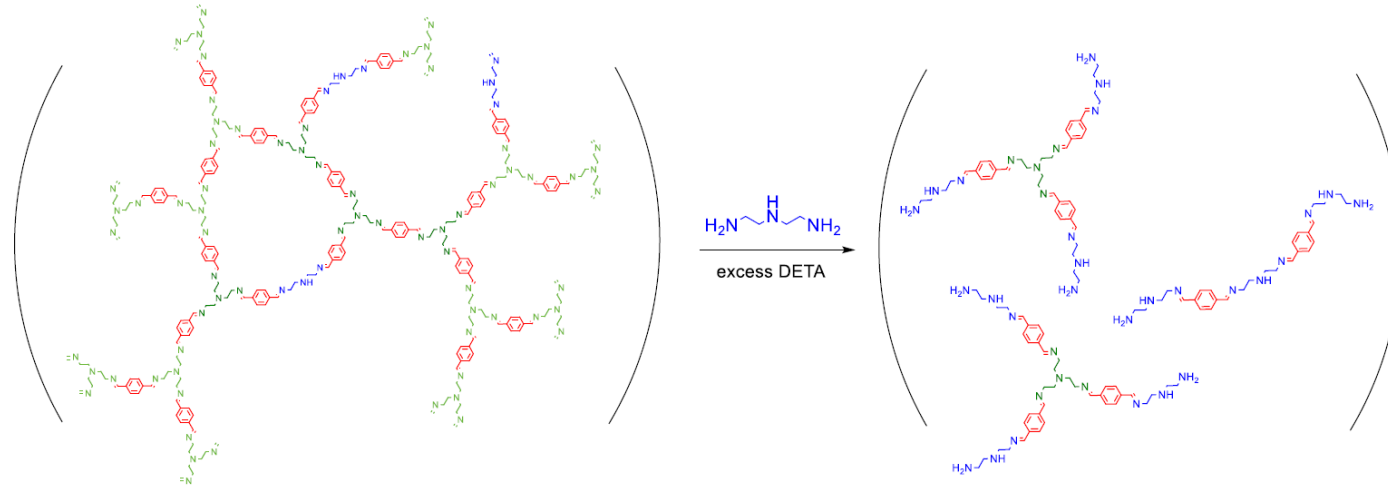


Pultrusion: 1 minute cure



Prepreg production: viscosity, pot-life

## Recyclability

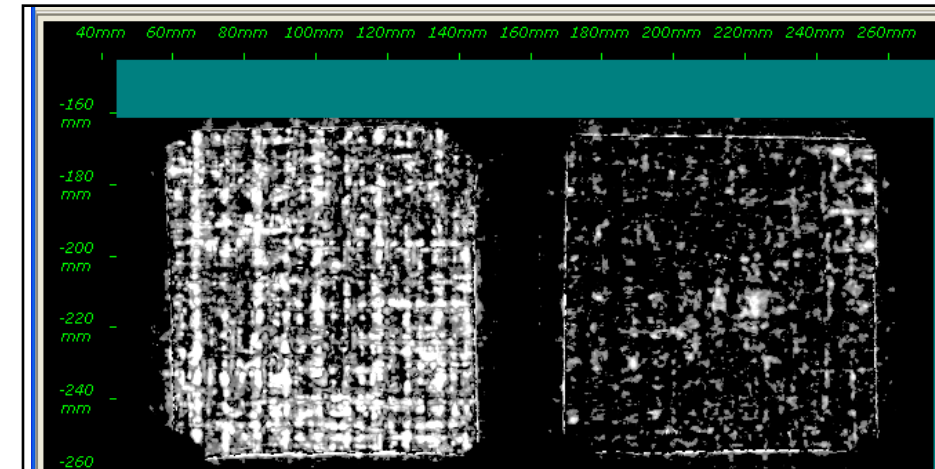


- Cure prepreg in line.
- Shelf stability.
- No wet chemicals.
- Dry Layup.
- Short dwell time.

# Approach - Acoustic analysis

## Optimize composite stamping process & establish Acoustic response

- Study the impact of temperature, time and pressure on interlaminar shear strength in consolidation of pre-cured vitrimer composite plies.
- Validate compression forming results in 3D part consolidation
- Use selected range of sub 1-minute stamping conditions for further study of ultrasonic response
  - Investigate correlation of bond strength with C-scan results by mapping samples, conducting short beam shear analysis in areas of interest.
  - Microscopic crosscut analysis to characterize defects
- **Reporting on Ultrasonic analysis**
  - Report analysis of material signatures and defects
  - Discuss limitations, potential and appropriateness of techniques
  - Report recommendations for technique refinement and future work



C-scan results in first period demonstrate good contrast range between well consolidated and poorly consolidated samples.

# Approach - Impact testing

## Impact & strain rate response

1. Interaction with OEM partner to guide targets & provide design & modeling baseline
  - redesign component for simplicity of production, lightweight, and simulated crash performance
  - produce tooling, validate compression forming process in a full-scale component mold.
2. Strain rate studies using Split Hopkinson Bar to understand material response vs. quasi-static.
  - re-run part-specific crash simulations using strain rate response data.
3. TMAC testing of test samples across strain rates.
  - re-run part-specific crash simulations using strain rate response data.



TMAC Machine

# Approach - Milestones

	Q4 2018		Q1 2019		Q2 2019		Q3 2019		Q4 2019		Q1 2020		Q2 2020		Q3 2020	
Resin development																
Composite development																
Preliminary testing - PNNL, SNL																
Compression forming development																
Acoustic analysis																
Split Hopkinson testing																
TMAC Testing																

## PROJECT OBJECTIVE

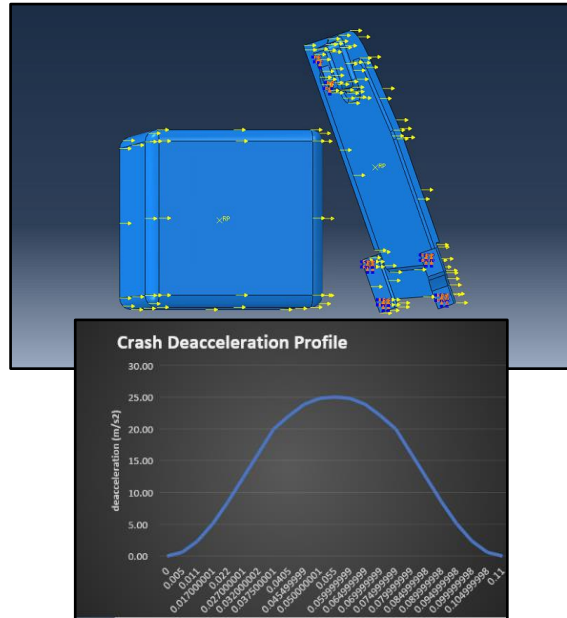
Manufacture seatback cover using Mallinda's vitrimer resin achieving reduced weight (OEM GMT part), reduced consolidation time, recyclability and passing OEM's crash retention test parameters.

## PROJECT DELIVERABLES

- Crash Retention Test (ANALYTICAL)
- Mold Design and Fabrication
- Prepreg Manufacturing
- Template Design for Part
- Template routing and curing
- Compression Forming
- Recycling Part

# Technical Accomplishment and Progress - OEM Seatback Cover

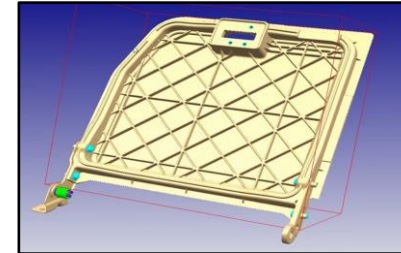
## CRASH-LUGGAGE RETENTION TEST



- The crash retention test was done for a luggage of dimension 300mmx300mmx300mm, weighing 20 Kg.
- The distance of 200mm was maintained between seatback and luggage.
- Number of plies used for Seat back : 16 (Unidirectional)

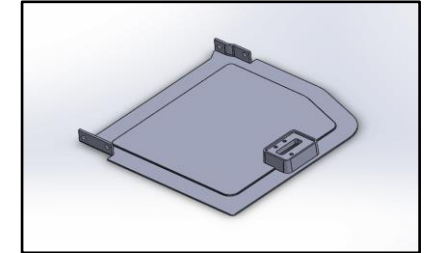
## CRASH-LUGGAGE RETENTION TEST RESULTS

OEM



- MATERIAL USED : GMT
- TOTAL VOLUME: 1600 cc
- APPROX. WEIGHT: 4.5 lbs.
- FIBER VOLUME: 45%
- NOT RECYCLABLE

MALLINDA

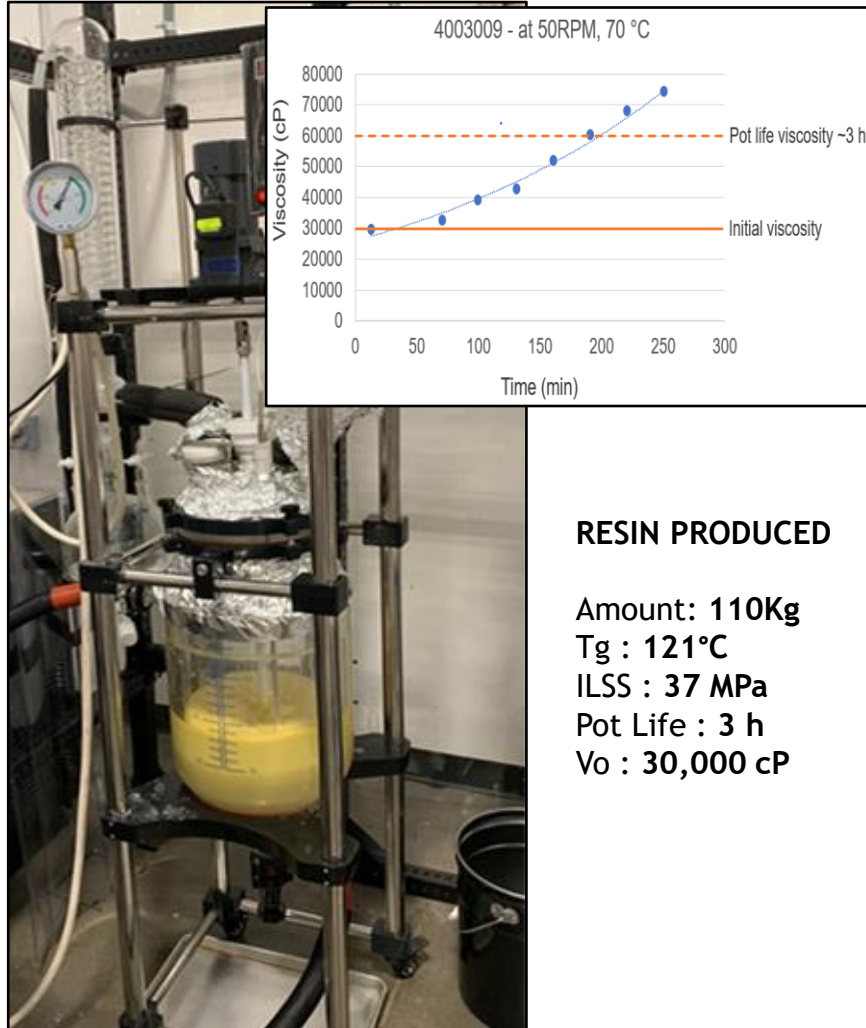


- MATERIAL USED : CF-PREPREG (MALLINDA)
- TOTAL VOLUME: 791.6 cc
- APPROX. WEIGHT: 2.5 lbs.
- FIBER VOLUME: 60%
- RECYCLABLE

- Maximum deformation permissible for seatback: 3.44"
- Mallinda maximum simulation seatback deformation: 2.408"
- Mallinda Seatback Volume reduction: 50.52%
- Mallinda Seatback Weight Reduction: 41.11%

# Technical Accomplishment and Progress - OEM Seatback Cover

## MALLINDA IN-HOUSE RESIN SCALE UP



### RESIN PRODUCED

Amount: 110Kg  
T<sub>g</sub> : 121°C  
ILSS : 37 MPa  
Pot Life : 3 h  
V<sub>o</sub> : 30,000 cP

## MALLINDA TOLL PREPREG MANUFACTURING



### PREPREG FABRICATED

Woven Carbon Fiber Prepreg, Resin Content 45%,  
60" wide, 100 LY.  
Fiber: Hexcel Hexforce 463  
Resin: Mallinda T130

Woven Fiberglass Prepreg, Resin Content 45%,  
60" wide, 100 LY.  
Fiber: 7781 E-glass  
Resin: Mallinda T130

# Technical Accomplishment and Progress - OEM Seatback Cover

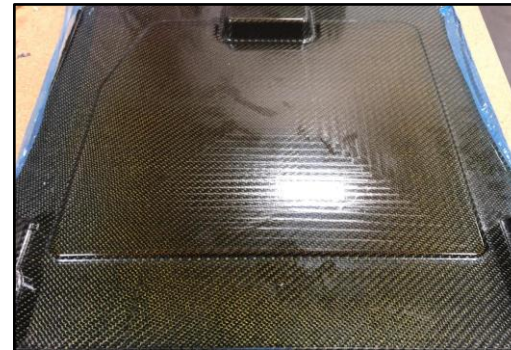
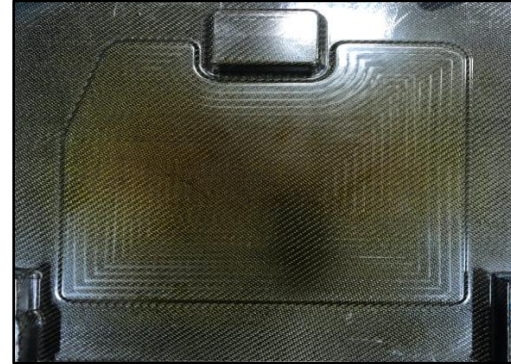
## MALLINDA COMPRESSION FORMING



Customized mold designed and  
fabricated for seatback cover  
compression forming.

## FINAL CONSOLIDATED SEATBACK PART

MALLINDA (CFRP)



OEM (GMT)



OEM(GMT) seatback weight: 2.279 Kg  
Mallinda (CFRP) seatback weight: 1.343 Kg  
Net Weight Reduction: **41.07%**

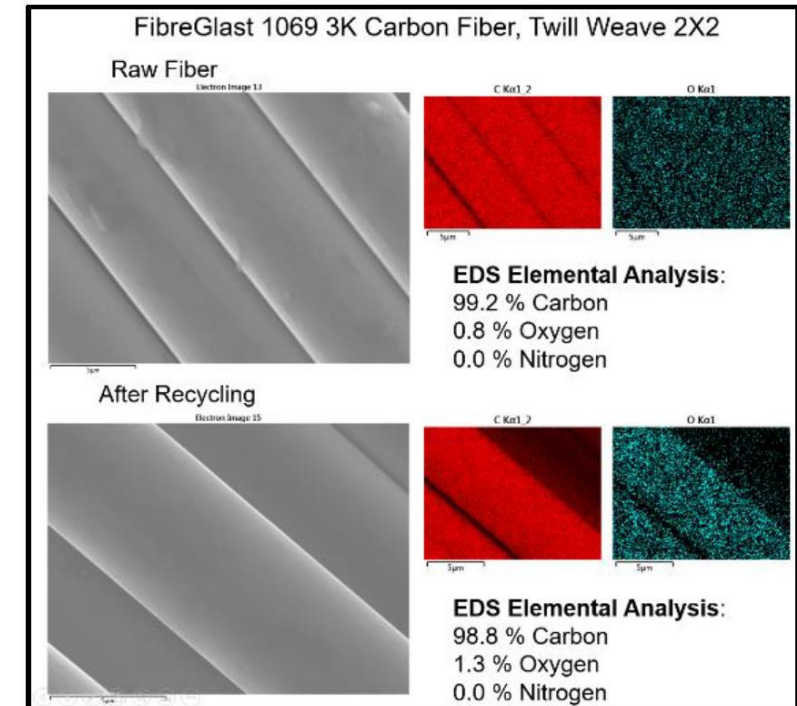
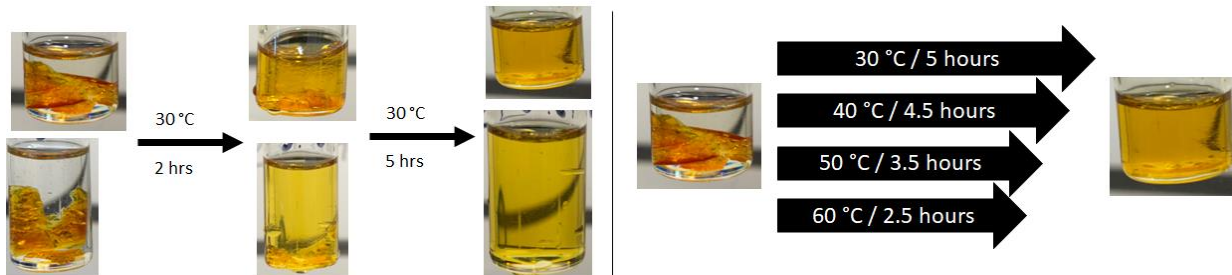
# Technical Accomplishment and Progress - OEM Seatback Cover

## RECYCLING



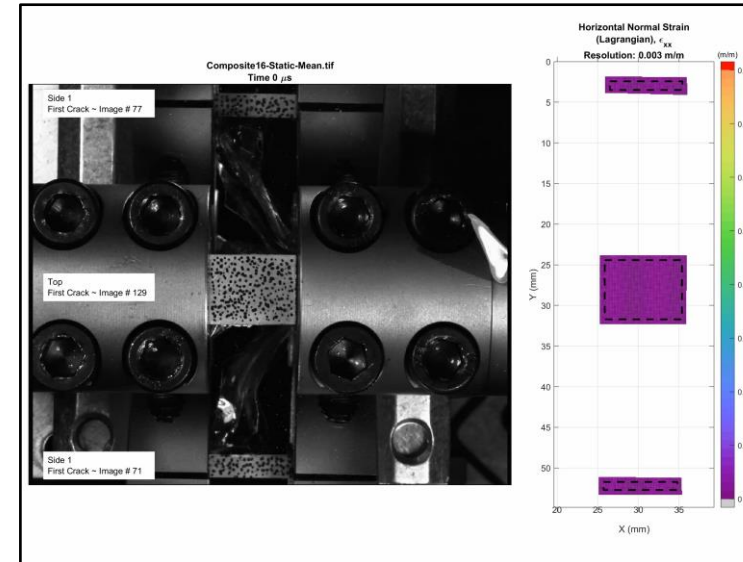
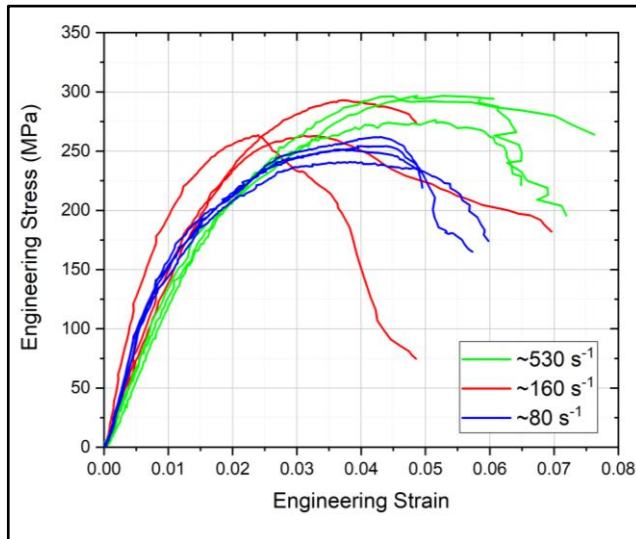
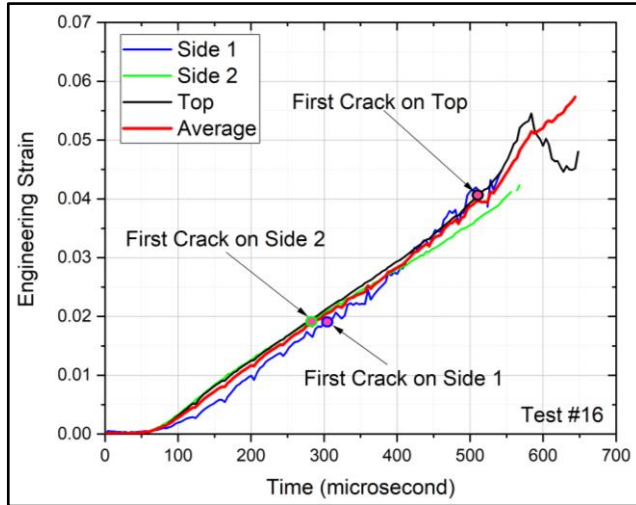
- Bench scale method development to improve recycling process for structural resin formulations
- Anticipated maximum resin in second iteration formulations: 41%
- SEM/EDS examination of surface of recovered carbon fiber materials
- Scale up of solution recycling to entire component (video)

## MALLINDA HEADLIGHT HOUSING RECYCLING



# Technical Accomplishment and Progress - Intermediate strain rate initial testing

## Dynamic Tensile Tests



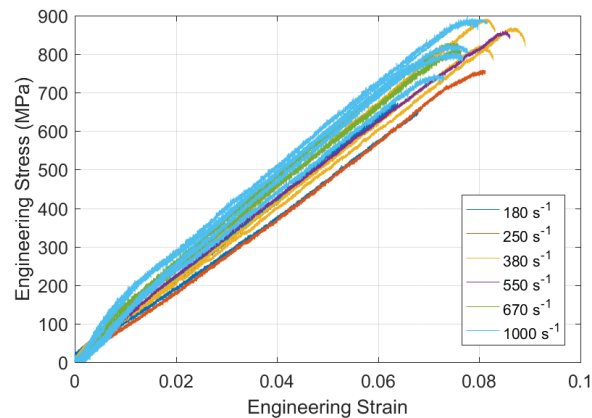
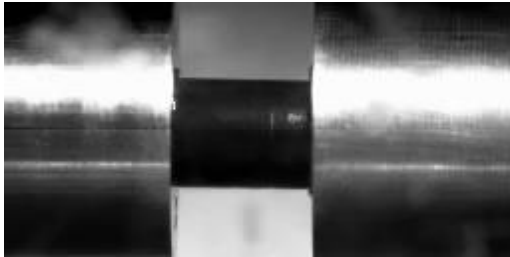
- The Dynamic Tensile test was performed under three strain rates of 80/s, 160/s and 530/s.
- The maximum Dynamic Tensile Strength ranges from 250MPa to 300MPa.
- The modulus had some outliers, although most of them remained constant within deviation with varying strain rates.
- These dynamic tensile test results show insignificant strain rate effect.

# Technical Accomplishment and Progress - Intermediate strain rate initial testing

## Dynamic Compression Tests

### Out of Plane

[Loading Direction Perpendicular to the Plate]

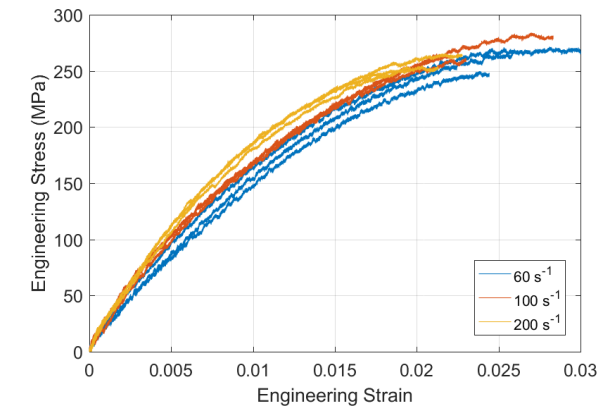
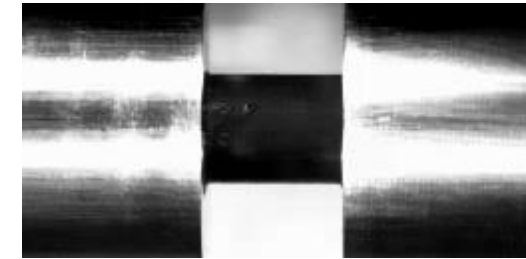


The dynamic Compression Tests were performed at varying strain rates of 180/s, 250/s, 380/s, 550/s, 670/s and 1000/s for out of plane tests.

- The dynamic compression strength ranged from **750MPa to 900MPa**.
- The modulus increases slightly with strain rates from **180/s to 1000/s**.

### In Plane

[Loading Direction along with the Plate;  
~45°/135° to the fibers]



The dynamic Compression Tests were performed at varying strain rates of 60/s, 100/s and 200/s for in plane tests.

- The dynamic compression strength ranged from **250MPa to 275MPa**.
- The modulus increases slightly with strain rates from **60/s to 200/s**.

# Technical Accomplishment and Progress -Time Temperature Pressure Study

	Time	Temperature	Pressure	Short Beam StrengthMPa
1	30	160	200	24.925
2	60	180	200	32.77
3	30	180	200	30.88
4	30	180	400	55.65
5	60	200	400	40.2875
6	60	160	100	29.5
7	300	200	400	50.925
8	600	160	400	53.3
9	600	180	100	51.84
10	300	200	200	43.7625
11	30	160	400	41.5
12	600	180	400	60.7
13	60	160	200	36.38
14	30	180	100	28.42
15	300	160	200	42.31
16	300	180	400	60.025
17	60	180	400	39.175
18	600	200	100	42.475
19	60	160	400	36.68
20	300	200	100	31.442
21	600	160	100	48.95
22	600	180	200	48.25
23	300	180	100	39.65
24	30	200	200	34.22
25	30	200	400	30.942
26	60	180	100	19.06
27	600	200	200	39.75
28	30	160	100	19.45
29	300	160	100	24.1
30	60	200	100	33.56
31	60	200	200	40.04
32	300	180	200	51.95
33	30	200	100	40.35
34	600	160	200	47.1875
35	600	200	400	45.425
36	300	160	400	57.6

**OBJECTIVE:** To understand the relationship between Temperature, Pressure and Time has on Short beam Strength of a Mallinda's consolidated laminate.



Temperature Samples(C):  
160 | 180 | 200



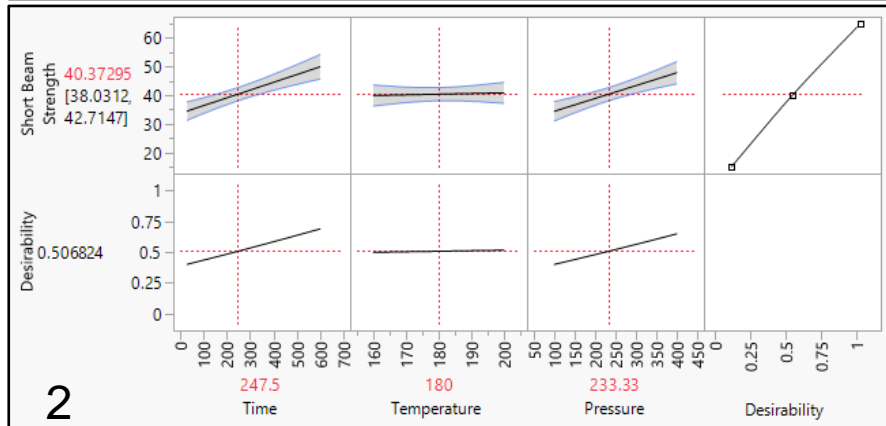
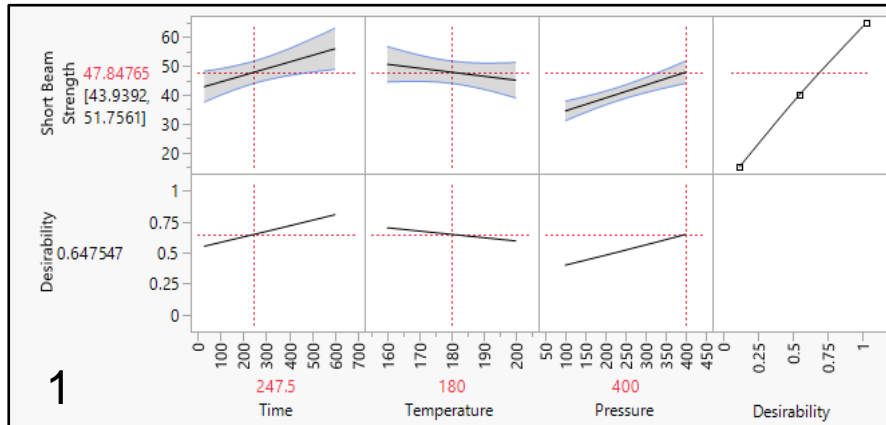
Pressure Samples (Psi):  
100 | 200 | 400



Time Sample Set (sec.):  
30 | 60 | 300 | 600

Number of Test Samples:  $4 \times 3 \times 3 = 36$

# Technical Accomplishment and Progress -Time Temperature Pressure Study



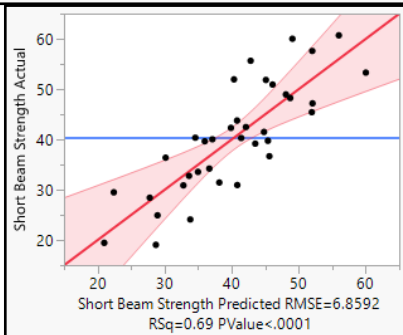
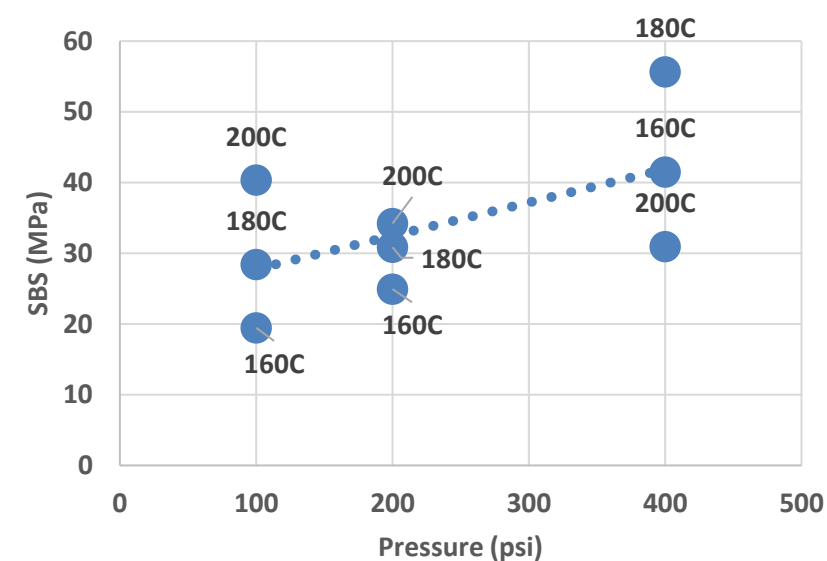
Short Beam Strength vs Time-Temperature-Pressure

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	18.95507	12.8918	1.47	0.1526
Time	0.0271413	0.004996	5.43	<.0001*
Temperature	0.0235344	0.070006	0.34	0.7392
Pressure	0.0448473	0.009166	4.89	<.0001*
(Time-247.5)*(Temperature-180)	-0.000556	0.000306	-1.82	0.0801
(Time-247.5)*(Pressure-233.333)	-2.438e-5	0.00004	-0.61	0.5476
(Temperature-180)*(Pressure-233.333)	-0.000972	0.000561	-1.73	0.0943
(Time-247.5)*(Temperature-180)*(Pressure-233.333)	2.2622e-6	2.453e-6	0.92	0.3642

- The Time & Pressure have significant effect on Short Beam Strength among the other parameters as can be seen In Prob |t| values in Parameter Estimates and slope of Desirability curves.
- We can achieve higher Short Beam Strength values by optimizing time and pressure parameters since they are heavy impact factors with a higher degree of confidence.
- As seen in figure 1 & 2, while keeping time to its optimized value and maxing out on pressure we achieved a higher SBS benchmark.

SBS vs Pressure after 30 seconds



# Response to previous reviewers' comments

## Concerns on approach:

1. Rate correlation of SHPB approach vs. alternative approaches appropriate test to project?
2. The use of hybrid fibers vs. baseline material characterization in CF & Glass.
3. Missing link of composite mechanics & modeling work to direct experimental design parameters.

## Concerns on Accomplishments and progress:

1. Poor communication of performance data.
2. Elaborate on baseline polymer properties
3. Study of temperature, pressure & time on bond strength recommended
4. More background on slides 11 & 12- how were the composites formed, composition, etc.

## Concerns on Collaboration:

1. Industry partner would help set targets

## Proposed future research:

1. Too vague- need specificity in metrics, and planned experiments

## Responses on approach:

1. Original rationale: Within the National lab system, TMAC & SHPB provide very different test metrics for probing strain rate response of the materials, which could enlighten future development efforts. Drop towers and falling dart impactors are relatively accessible outside of the LightMat consortium, and needn't be included in the lightMat funded efforts. SHPB results have provided relevant insights into automotive crash simulations.
2. Original rationale: Intriguing literature reports on hybrid fibers and recent commercial availability of hybrid fabrics could provide a design path to tailoring strain rate response. In line with reviewer comments, the project team has found that the project resources are not sufficient to study hybrid fabrics, and will focus on characterization of CF and GF materials. The reviewers' point of composite mechanics work being a major missing piece in the initial experimental design is well founded.
3. The reviewers' point of composite mechanics work being a major missing piece in the initial experimental design is well founded.

## Responses on Accomplishments and progress:

1. The PI agrees that there was poor communication in the first presentation, and has tried to address that.
2. Baseline resin & composite properties had been developed & established prior to the present work, but are herein presented as technical background
3. The PI agrees with the reviewer comments, and as planned, but as poorly communicated, the project team has carried out a study of temperature time & pressure on interlaminar shear strength
4. Slides 11 & 12 in the previous presentations were not stock images, but real photographs of hybrid fabrics and vitrimer composites acquired and prepared specifically for this study. Details about the material characterized by C-scan is provided in the technical back-up slides.

## Responses on Collaboration:

1. The PI agrees that vehicle industry partners would provide direction to the project.

## Proposed future research:

1. The PI agrees that the planned experiments were poorly communicated, and has tried to address that issue in this presentation.

# Collaboration & Coordination



**Pacific Northwest National Lab:**  
Leading Acoustic method development  
-Michael Larche/ Leo Fifield



**Sandia National Lab:**  
Leading split Hopkinson bar high speed testing  
-Bo Song



**ORNL:**  
Leading TMAC testing  
-Robert Norris

# Remaining Challenges & Barriers

- Early in the fundamental understanding of vitrimer materials, and much remains outside the scope of the present work
- Too many variables which potentially effect impact response to effectively optimize material properties within the scope of the project, as was initially intended. Per the reviewer comments, composite mechanics simulation would partially help to remedy this problem

# Proposed Future Research

- Add C-scan analysis to temperature, time, pressure study, to correlate scan reads to quantitative shear strength, and investigate & characterize defects via crosscut microscopy.
- Complete intermediate strain rate response study & use results to inform crash simulation. Finish impact work with TMAC study of composite structures.
- Based on optimized consolidation conditions, demonstrate sub 1-minute in-mold dwell for 3D part production.

Any proposed future work is subject to change based on funding levels

# Summary

## PREVIOUS KEY TAKE AWAYS

- Malleable thermoset resins reformulated to meet the specific challenges of hybrid fiber composites
- Initial samples & preliminary testing performed for Acoustic & High-Speed Impact testing
- The bulk of the project remains ahead. Essential questions of acoustic analysis of malleable consolidation efficiency & the efficacy of hybrid fabric composites in constraining crash failure modes remain untested.

## KEY TAKE AWAYS

- Mallinda Inc. successfully developed a high Tg resin system for automotive application.
- Mallinda Inc. manufactured in-house scaled production of resin and tolled 200 linear yards of prepreg.
- The 3-minute in mold compression forming was performed to produce an OEM automotive part.
- Complete recycling of part into resin and fiber was successfully demonstrated.
- Initial intermediate strain dynamic tensile and compression tests revealed mild strain rate response.
- The Time-Temperature-Pressure parameters were systematically studied to determine impact of each variable on vitrimer weld-strength as determined by short beam shear testing. While both time and pressure have a positive impact on bond strength, temperature is more dynamic, and must be optimized.

# Technical Back-up Slides

# Technical Progress- Summary of prior results

## Initial resin development for hybrid fiber- UHMWPE

- Fiber- and tool-limited compression conditions
- Glass transition temperature in range
- Minimum Interlaminar shear strength (ILSS)
- Maximum moisture absorption (2 h boil)
- Adhesion to ultrahigh molecular weight polyethylene (UHMWPE)

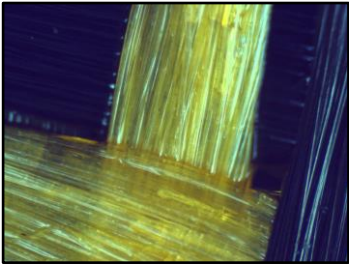
### Efforts:

- >70 unique formulations prepared

### Accomplishments:

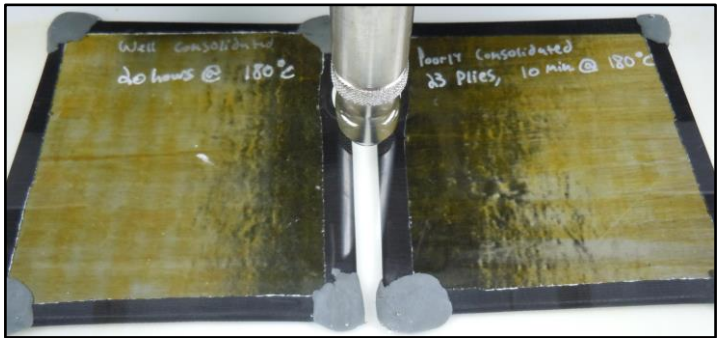
- Successful initial resin development
- Hit target
- Impregnates UHMWPE fibers well

Requirement Description	Specification	Uni Fiber	Dyneema Fiber
Cure Temperature	<125 °C	115 °C	115 °C
Consolidation Temperature	≤ 125 °C	125 °C	125 °C
Consolidation Pressure	≤ 500 psi	500 psi	500 psi
SBS	45 MPa	50 MPa	28 MPa
Tg	< 125 °C	110 °C	110 °C
Moisture Uptake (boil test)	< 2%	1.82%	1.82%

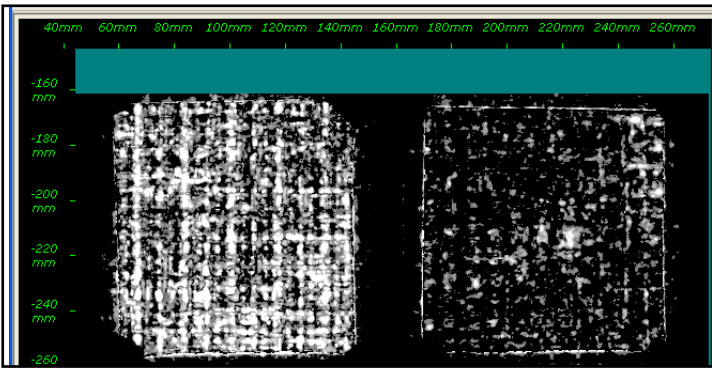


50% v/v resin, CF UD 2585-12K

23 layers, 180C, 20 h, 15 psi (L), 23 layers, 180C, 10 minutes, 15 psi (R)



## 10 MHz C-scan Results

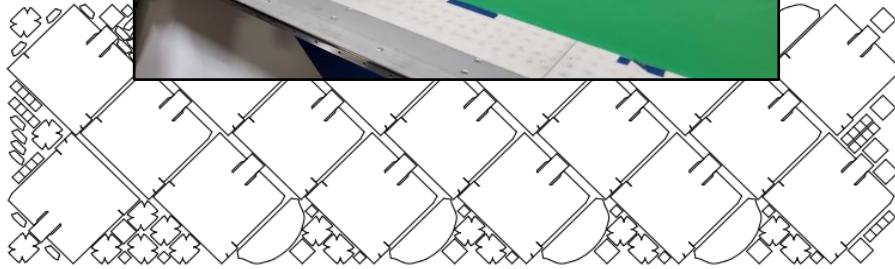
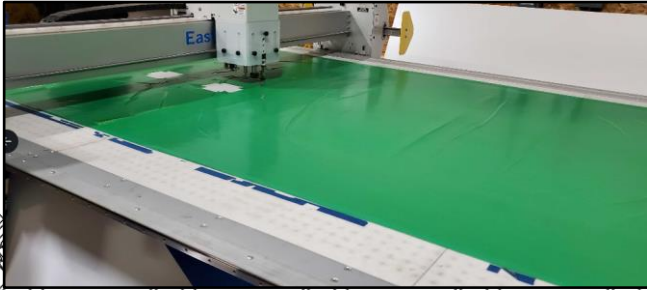


### Initial C-scan results

- 10 % 20 MHz Ultrasonic transducers in pulse echo mode
- Examination focused through plate near the back surface
- Contrast between well & poorly consolidated samples shows good contrast to move forward with quantitative experiments

# Technical Accomplishment and Progress - OEM Seatback Cover

## MALLINDA TEMPLATE ROUTING



### *0/90 orientation:*

44 Main  
132 Wings  
44 Deep Draw  
25 Headlight  
132 2"x2" Lab Samples  
22 4"x4" Lab Samples

### *45/45 orientation:*

45 Main  
126 Wings  
44 Deep Draw  
24 Headlight  
129 2"x2" Lab Samples  
40 4"x4" Lab Samples

## MALLINDA PLY CURING



- The individual templates were cured in a walk-in oven.
- With 2 racks, >48 plies were cured simultaneously.
- The plies were cured at 150°C 1 h, then 180°C 1 h.

# Technical Accomplishment and Progress - OEM Seatback Cover

## SIMULTANEOUS CONSOLIDATION OF HEADLIGHT HOUSING AT MALLINDA

In-mold dwell time demonstrated: 3 minutes,  
temperature: 180 C, Pressure: 50 psi



Pre-cured vitrimer  
prepreg sheets

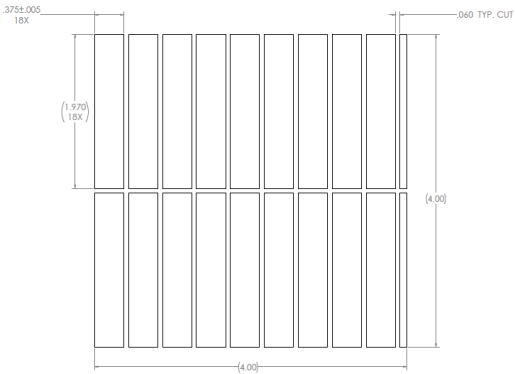
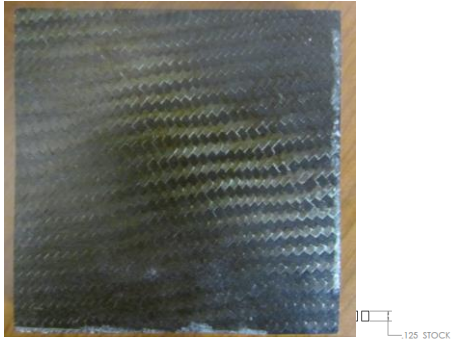


CFRP vitrimer parts  
produced in 3 minute  
dwell time



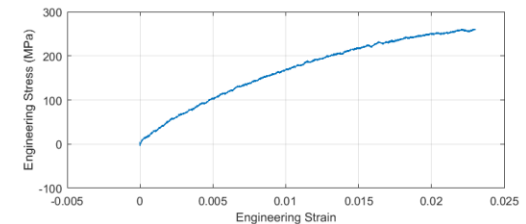
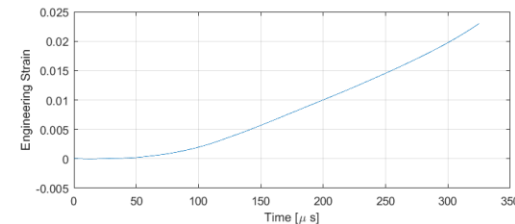
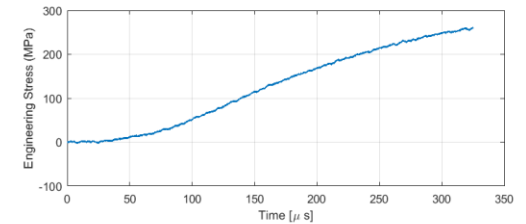
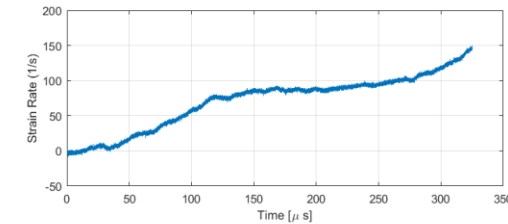
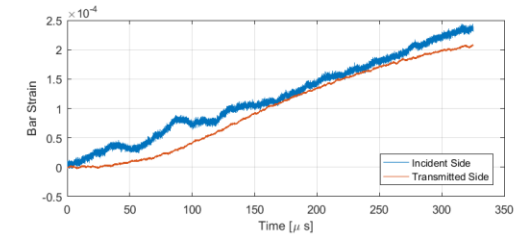
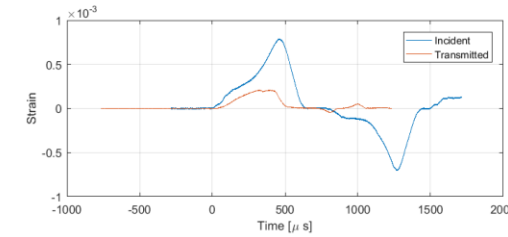
GFRP vitrimer parts  
produced in 3 minute  
dwell time

# Technical Accomplishment and Progress - Intermediate strain rate initial testing



## Kolsky Tension bar & Kolsky Compression bar tests Intermediate strain rate response

- ❖ **Tensile Specimen**
  - Gage section:  
~12 mm (L) X 3.42 mm (T) X 9.46 mm (W)
  - Loading direction is ~45/135 degree to the fiber direction
- ❖ **The tensile specimen was gripped with specimen holder with a layer of sand paper (for increasing friction)**
- ❖ **Compression Specimen**
  - Gage section:  $\Phi 9.9$  mm X 12.7 mm
  - Loading direction is
    - Perpendicular to the plate (out of plane)
    - Along with the plate (in plane)  
~45°/135° to the fibers



Pulse shaping for dynamic stress equilibrium and constant strain rate is challenging

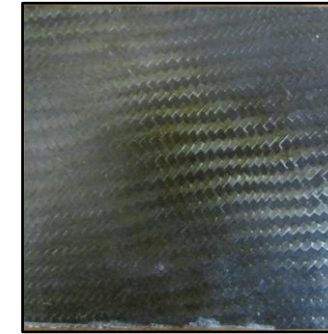
- There exist strain-rate limits for Kolsky bar tests depending on specimen failure strains

# Technical Back-up Slide

## - LightMAT Project

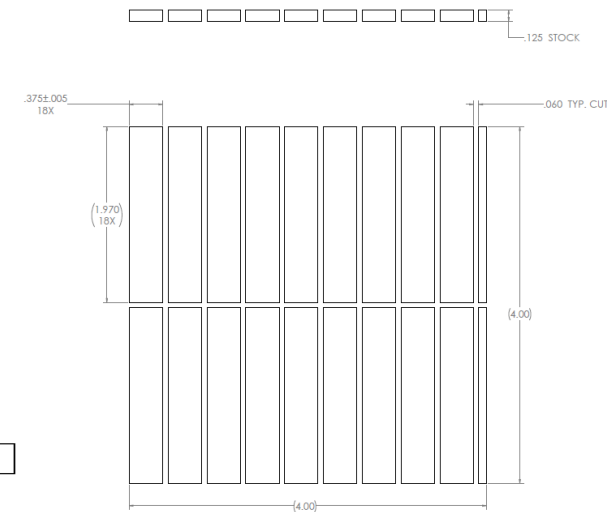
### SPECIMEN DIMENSIONS

- The specimen dimensions are based on ASTM 3039; straight specimen design.
- The tabbing is glued to the surface to provide grip at interface.
- Specimen: 2 x 2 Twill weave fabric
- Plate thickness 1/2".



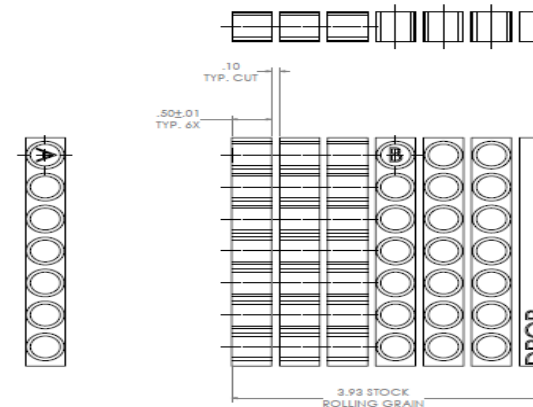
### DYNAMIC TENSILE TEST

- Gage section: 12 mm (L) X 3.42 mm (T) X 9.46 mm (W)
- Loading direction is: 45/135 degree to the fiber direction.
- The tensile specimen was gripped with specimen holder with a layer of sandpaper (for increasing friction).



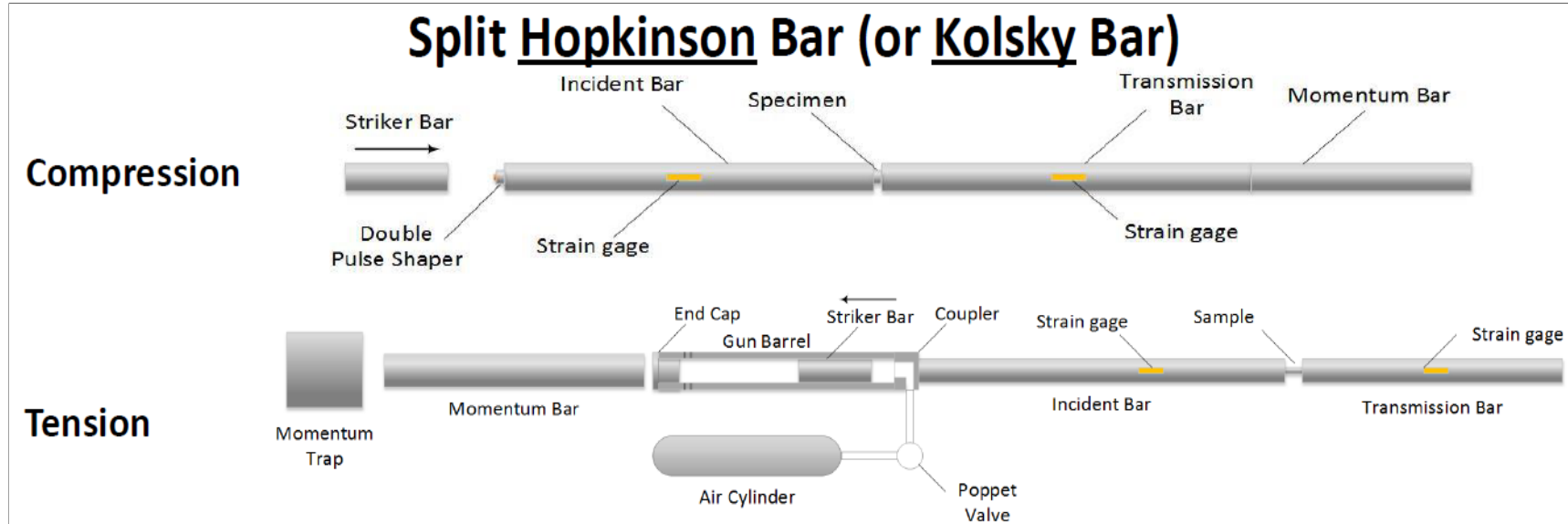
### DYNAMIC COMPRESSION TEST

- Gage section: Φ9.9 mm X 12.7 mm
- Loading direction is Perpendicular to the plate (out of plane)
- Along with the plate (in plane): 45°/135° to the fibers

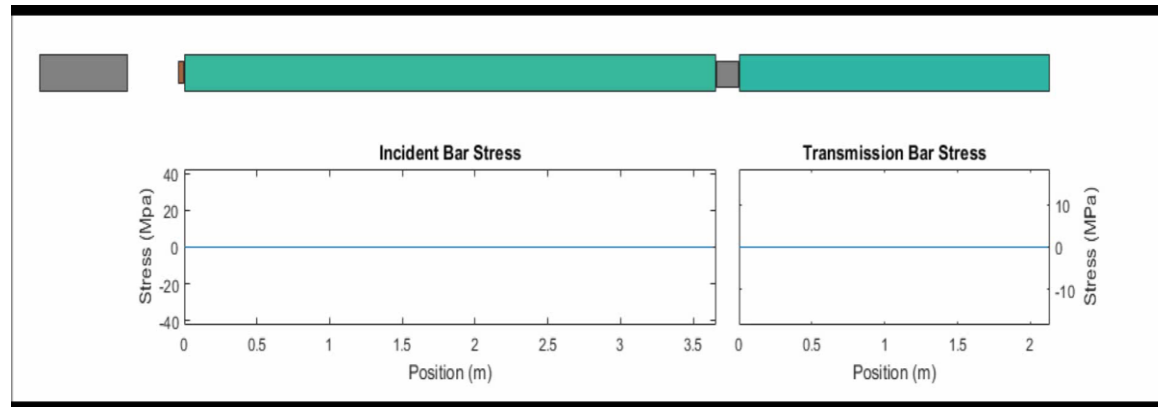
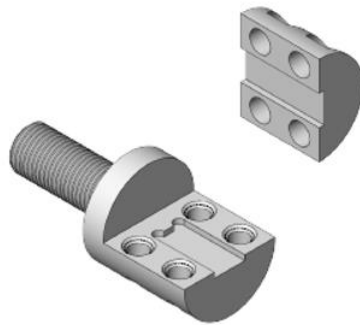


# Technical Back-up Slide - LightMAT Project

## TEST SETUP



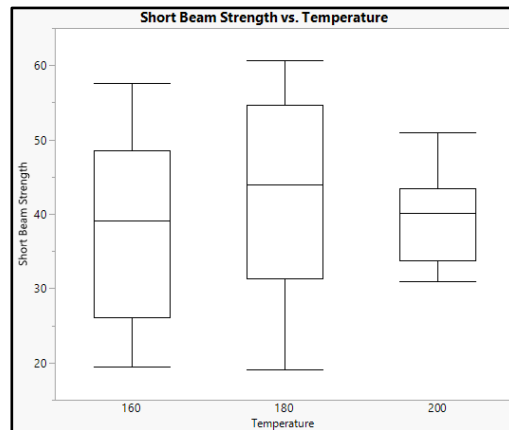
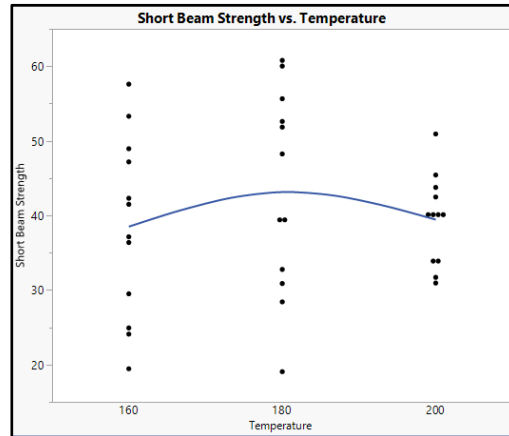
Sample Holder Design



# Technical Back-up Slide

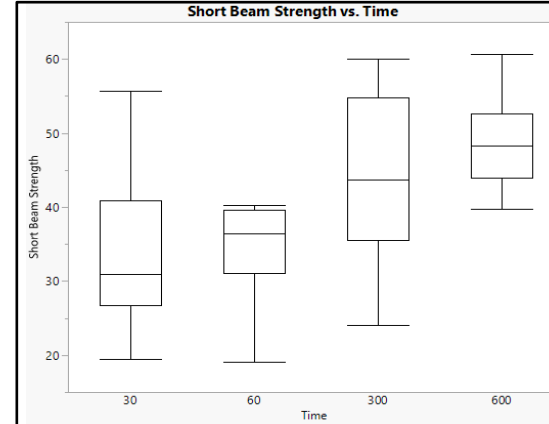
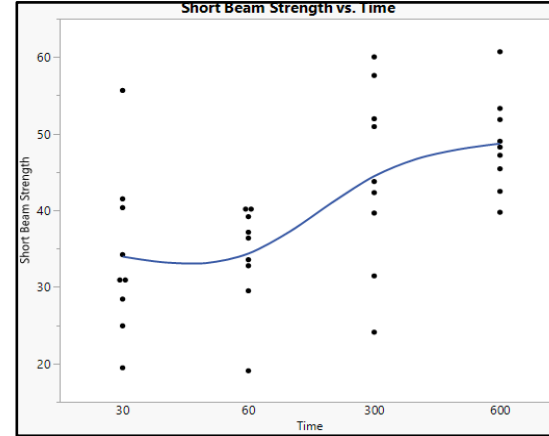
## -Time Temperature Pressure Study

### Short Beam Strength vs Temperature



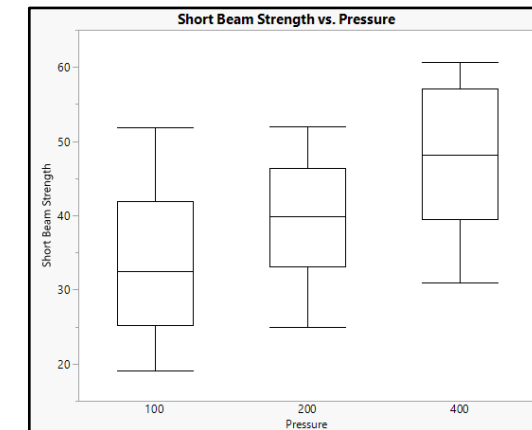
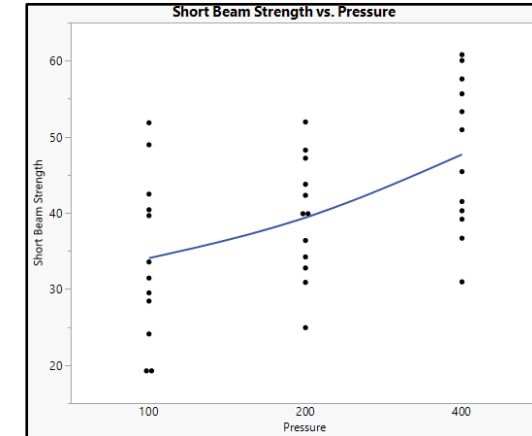
The SBS increases with temperature from 160C to 180C and drops down from 180C to 200C.

### Short Beam Strength vs Time



The SBS values increase with time from 30/60 to 300/600 seconds. However they remain relatively consistent from 30-60 and 300-600 seconds.

### Short Beam Strength vs Pressure

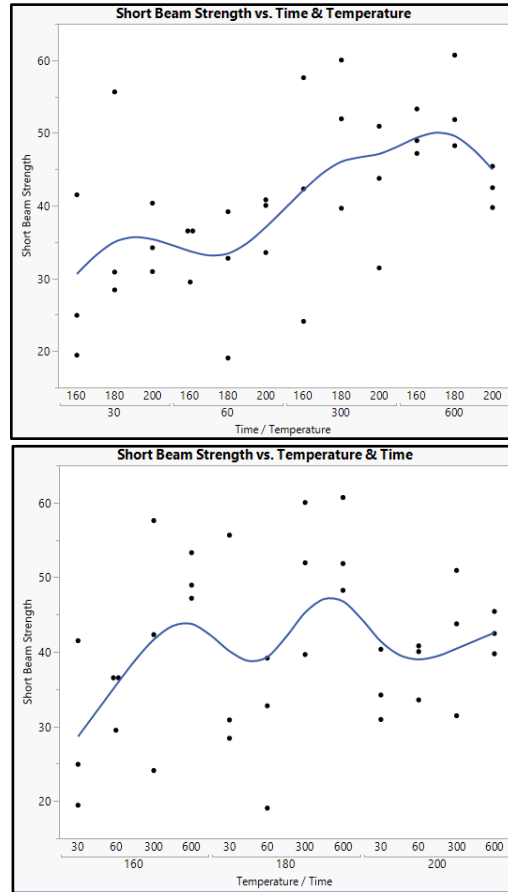


The SBS trends to increase with Pressure almost linearly.

# Technical Back-up Slide

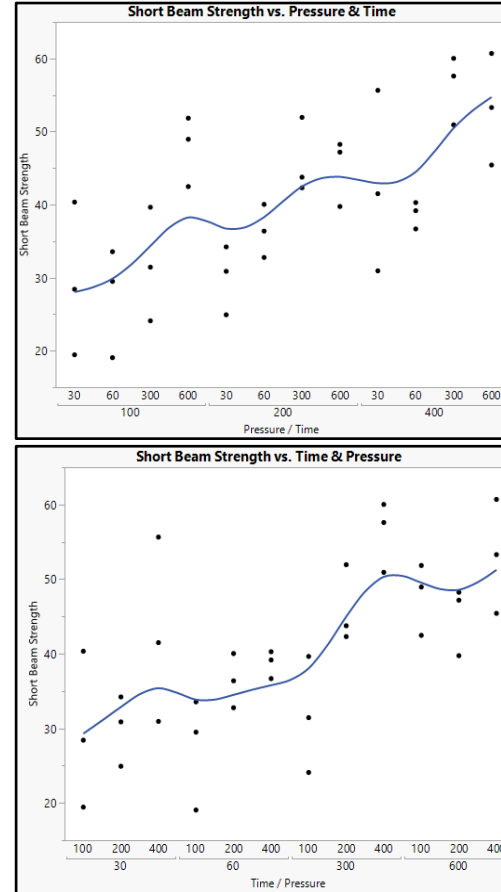
## -Time Temperature Pressure Study

### Short Beam Strength vs Time-Temperature



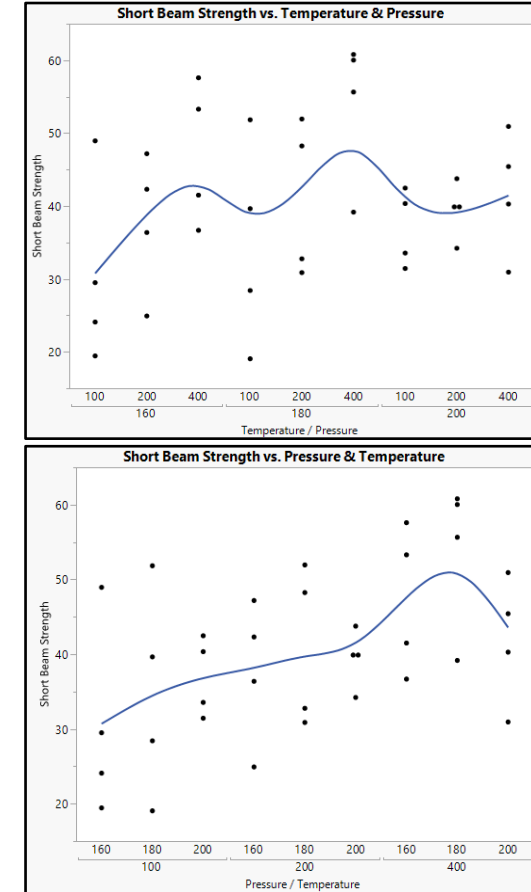
The SBS peaks at 180C for all time stamps with exception of 60 seconds.

### Short Beam Strength vs Pressure-Time



SBS increases linearly with both time and temperature.

### Short Beam Strength vs Temperature-Pressure



SBS increases gradually with pressure and we see a dip in SBS at higher temperature.